

Studies on the Recovery of Essence from Florida Orange Juices^a

DONALD A. MORGAN AND M. K. VELDHUIS

U. S. Citrus Products Station,^b Winter Haven, Florida

AND

R. K. ESKEW AND G. W. M. PHILLIPS

Eastern Regional Research Laboratory,^b Philadelphia, Pa.

A system for recovering water-soluble essences of orange juice under vacuum at temperatures of 110-115° F. (43.3-46.1° C.) is described. The orange juice is not noticeably deteriorated at this processing temperature. A relationship is shown between aroma of the essence and peel oil content. The use of water-soluble essence enhanced the floral character of freshly prepared concentrate and reconstituted product.

In the process of concentration of citrus juices, certain water-soluble odorous constituents which are characteristic of the fresh juice are normally volatilized along with the water. The concentrate when reconstituted, therefore, lacks natural aroma. Methods of restoring this lost flavor are of interest to food technologists.

In any study of the flavor of citrus juices, peel oils need also to be considered, since they are known to contribute to the characteristic aromas. Cold pressed orange peel oil, for example, has been used to impart an orange flavor to confectionery and beverages, including orange concentrate (8, 15).

Principal objective of the present work was to determine the effectiveness of water-soluble, steam-volatile constituents in enhancing the flavor of the orange concentrate. The investigation also comprises the adaptation and improvement of equipment developed by other workers (4, 5) for the recovery of volatile constituents from fruit juices, and an evaluation of the odor strength of the essence recovered and its use for restoring odor to concentrate. The term essence as used in this paper refers specifically to the water layer. It is realized that odorous materials present will be partitioned between the aqueous phase and a possible oil phase predominately *d-limonene*.

PREVIOUS WORK

Chemical composition. Hall and Wilson (7) studied the chemical composition of the volatile water-soluble, aromatic constituents which they concentrated from orange juice by successive vacuum distillations. Oils which separated were systematically discarded. The constituents found would also be present in essence recovered in the current study because of basic similarity in the recovery processes. Ethyl alcohol, acetone, acetaldehyde, and formic acid were the principal constituents, with ethyl alcohol being the most abundant. An olefinic alcohol, an amyl alcohol, phenylethyl alcohol, and esters of formic, acetic, and caprylic acids were also present; some terpenes were indicated.

^a Presented at the Twelfth Annual Meeting of the IFT at Grand Rapids, Michigan, June 9, 1952.

^b One of the Laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

Poore in 1932 (14) investigated the composition of California Valencia and Washington Navel orange oil and reported the presence of *d*-limonene, decylic aldehyde, formic acid, acetic acid, capric acid, caprylic acid, octyl alcohol, and an olefine alcohol, $C_{10}H_{18}O$, closely related to linalool. A trace of linalool was also indicated. Nelson and Mottern (13) found citral in Florida Valencia orange oil. In the preparation of coldpressed oils such as these, an emulsion of oil in water or juice is obtained and the oil separated by centrifuging. Some of the peel oil constituents are water-soluble and steam-volatile. These constituents would be recovered as essence from the orange juice or water in which they are dissolved.

Rice, Keller, and Beavens (15) have studied the aromatic constituents in California orange juice. They rectified the water condensate obtained during concentration of the juice and used it to fortify the flavor and aroma of the concentrates produced. Upon storage of these concentrates, "apricot-like" flavors were reported in the reconstituted juices.

After extracting the water condensate with ether, only formaldehyde, methyl alcohol, acetaldehyde, ethyl alcohol, acetone, furfural, and an unidentified acetate ester were found. From 0.004 to 0.006% recoverable oil was found in juices which had been prepared from carefully peeled fruit. They concluded that the volatile flavor and aroma were primarily associated with the volatile oils and that the volatile flavor and aroma lost during evaporation could be restored by adding carefully selected coldpressed peel oil or orange puree.

Hydrogen sulfide was identified as one of the volatile constituents of orange juice by Kirchner, Rice, Miller, and Keller (9). Hydrogen sulfide would not be recovered in essence recovery under vacuum unless liquid air traps or some similar system were used.

Methods of restoring flavor. MacDowell, Moore, and Atkins (10) investigated the addition of fresh juice as a method of restoring flavor to orange concentrate. This method, known as the "cutback process," is now widely used. Some of the basic features of this method are incorporated in a patent assigned to the Secretary of Agriculture (10).

Kaufman and Campbell (8) have investigated the effect of variation in source of orange flavor and aroma on the flavor and aroma of reconstituted orange concentrate. They used the first condensate from atmospheric concentration of orange juice, a rectified condensate from vacuum concentration of orange juice, and various orange peel oils. They observed an "apricot- or strawberry-like" flavor after storage of frozen orange concentrates fortified with rectified condensate.

Methods of recovery. The method of recovering volatile aromatic constituents that has been singularly successful has been that developed at the Eastern Regional Research Laboratory, for use with apple juice (6, 11) and with grape juice (5). Other developments in this method have been accomplished at the Western Regional Research Laboratory (16). In these processes, the general procedure has been to heat the juice rapidly to the boiling point and then vaporize about 10% in a single pass through a tubular heat exchanger. Then, by fractionating the vapors in a packed column, a concentrated essence was obtained of about one-hundredth the volume of the original juice. The comparatively short heating period did not materially affect the flavor of these juices and excellent, full-flavored concentrates were prepared.

An effort was made at the U. S. Citrus Products Station, at Winter Haven, Florida, to adapt the essence recovery equipment

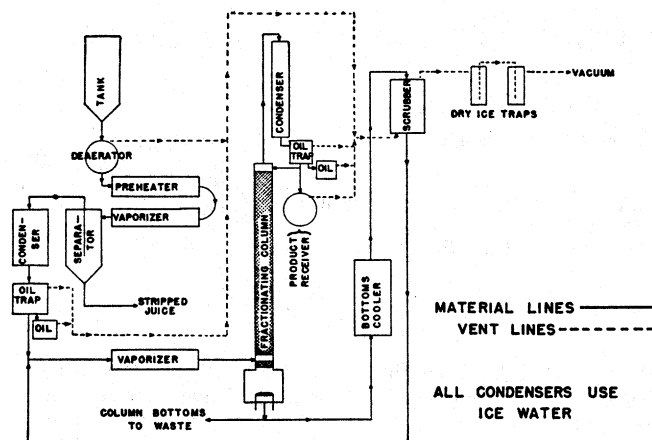


Figure 1. Flow diagram of essence unit.

originally developed at the Eastern Regional Research Laboratory to the preparation of full-flavored concentrated orange juice. The adaptation consisted of an oil decanter to remove the water-insoluble oils. It was found that the heating to boiling at atmospheric pressure materially affected the flavor of the stripped juice. However, an aromatic water-soluble essence, floral in character, was obtained. When stored in bottles at 35° F. (1.7° C.) for 5 years, these essences of 100- to 150-fold strength did not change materially.

A further adaptation was made at the Fruit and Vegetable Products Laboratory (USDA) at Weslaco, Texas. This adaptation consisted of cooling the heated juice rapidly by evaporation into a vacuum. Using this method, an aroma of grapefruit and Meyer lemons was obtained without serious deterioration of the juice. Each citrus variety yielded a distinctive essence.

EXPERIMENTAL

Equipment and operation. In the present investigation, equipment was used in which the juice was not heated above 115° F. (46.1° C.) and the heating, evaporation, and essence recovery were conducted entirely under vacuum. Figure 1 is a flow sheet of the method used in recovering essence in these experiments. Orange juice was pumped through a small diameter, jacketed tube where it was heated to about 115° F. (46.1° C.), and then about 10% of the liquid was vaporized in a second, larger jacketed tube. The liquid and vapors were immediately separated, the liquid being cooled to about 80° F. (26.7° C.) by flashing into a suitable vacuum after passing through a manually operated liquid seal. The vapors were condensed and any oil globules separated in a decanter. This condensate was again stripped by vaporizing about 30% of the liquid in another tubular heat-exchanger. These vapors led into the fractionating column where the aromatic materials were concentrated. The fractionating column had a stripping section between the vapor inlet and the reboiler of about one-tenth the length of the column. The vapors from the top of the column were condensed with a surface condenser and any oil globules again removed with a decanter. A portion of this condensate was removed continually as 100- to 150-fold essence and the remainder returned to the top of the column as reflux. Stripped column bottoms were removed substantially free of aromatic materials. All vent lines led to a manifold where the exit gas was scrubbed with refrigerated column bottoms. The enriched scrubbing liquid was mixed with condensate passing to the second vaporizer and so recycled. All gases and vapors passing through the scrubber were led through dry ice traps to remove additional vapors. Ice water was used in all condensers and coolers and hot (150° F. or 65.6° C.) water in all heaters and vaporizers. During operation, observations of rate of flow of juice, extent of vaporization in each of the 2 vaporizers, temperatures of vaporization, and pressures were recorded. The concentrated essence condensate in the dry ice traps, and column bottoms were collected separately and measured.

Ten gallons of fresh juice was the usual amount used for each run. The feed rate of fresh juice was maintained at about

8 gallons per hour and the essence volume at about 0.7% of the raw juice. A known volume of raw juice was used and stripped juice was determined by difference.

When concentrates were to be prepared for flavor evaluation, the stripped juice passed directly into a falling film evaporator and was concentrated to the desired solids content at 70° F. (21.1° C.).

Materials and preparation. In one series of experiments, juices of different peel oil contents were obtained from a single lot of Pineapple oranges. Included were: whole fruit puree, machine-reamed, hand-reamed and juice free of peel oil. The whole fruit puree (1, 2) was prepared by cutting fruit in quarters and passing through a tapered screw press with 0.027 inch perforations. Pulp, peel, and seeds were discarded. The machine-reamed juice was prepared on a rotary juice extractor of commercial design and the hand-reamed juice by cutting the fruit in halves and reaming by hand with an electric burring reamer. The juice free of peel oil was prepared by the method suggested by Blair and co-workers (3) in which the fruit was first plumped by immersing in water at 180° F. (82.2° C.) for 5 minutes, cooled, peeled by hand, the peeled fruit treated with permanganate to remove traces of peel oil, and with sodium bisulfite to remove permanganate stains. The fruit was then washed and the juice was extracted from the whole fruit in a tapered screw press with a 0.027 inch screen. Each of the stripped juices was passed through the essence unit a second time, the essence and trap condensates from each pass being collected as separate fractions.

A coldpressed peel oil emulsion also was used in the equipment. Emulsions of a good grade of orange peel oil were prepared at levels of 0.01% and 0.05%. The emulsions were passed through the equipment only once and the essence and trap samples collected.

Analytical methods and data. Recoverable oil contents, soluble solids, and total acid contents were determined on all fresh juices and recoverable oil again on the stripped juice.

The raw juice had a soluble solids content of 11.6° Brix and an acid of 0.90%. The range of recoverable oil was from 0.88% to 0.004%. The values of recoverable oil for machine-reamed and hand-reamed juices are considered normal for commercial operation. Grade A canned juice specifications call for not more than 0.03% recoverable oil and around 0.01% is generally considered satisfactory for reconstituted frozen concentrates. Values above 0.070% would be exceptional with current juice extraction procedures. The puree was included as an extreme.

The recoverable oil value in the juice free of peel oil was 0.004%. This oil presumably came from the fruit pulp since the peel had been carefully removed. The value of recoverable oil in juice prepared in this manner appears to vary widely with the maturity and perhaps also with the variety. Similar results were obtained by Rice, Keller and Beavens (15). In other work, with midseason Valencia oranges, this method yielded a juice of 0.0012% recoverable oil, and with late season Valencia oranges, recoverable oil value of 0.0006%.

EVALUATION

Methods. Attempts were first made to evaluate the strengths of the various essences by chemical methods. The permanganate oxidation procedure used in determining Oxygen Consumed values for sewage and modifications were tried. It was found that the values obtained were due largely to ethyl alcohol in the essence. Since alcohol is considered a minor factor in orange aroma and is not exclusively related to odor strength, the method was abandoned.

Approximations of the potencies of the various essences, trap condensates, peel oil emulsions, and orange juice were made by the odor threshold method (12). All the essence fractions were first reduced by dilution with distilled water until they occupied the same volume as the juice from which they came. The essences were then diluted in steps in clean glass stoppered bottles until a difference in odor could no longer be detected between the sample and distilled water. Steps in dilution used were: 10, 20, 40, 100, 125, 200, 333, 500, 1000, 1250, 2000, 3333, and 5000 to 1. Samples were always vigorously shaken before evaluation by smelling. The last dilution at which odor could

be detected (expressed as parts of solution per part of essence) was called the threshold value. A panel of 8 to 12 judges was used. Generally, 4 samples were judged at one time. However, a larger group could be judged since at the high dilutions used, the nose recovers from fatigue rapidly. Comparisons were made only between the 4 samples or less examined as a group. The threshold values obtained by the individual members of the panel were averaged for each sample. The sample with the greatest threshold value (the strongest odor) was arbitrarily assigned a value of 1.0 and the others in the group rated according to this value.

Comparisons made. Comparisons were made between odor threshold values of fresh orange juice and coldpressed peel oil emulsion of the same recoverable peel oil content; between odor threshold values of essence and coldpressed peel oil emulsions of known peel oil contents; and between odor threshold values of essence derived from fresh juice and essence from coldpressed peel oil emulsion of comparable peel oil content.

Comparisons of flavor of orange concentrates, with and without essence, to which peel oil had also been added were made. Essence was added so that it would be in the same proportion in the reconstituted juice as in the fresh juice from which it was obtained. Coldpressed peel oil was added to give a peel oil content of 0.010% v/v based on the reconstituted juice. Care was taken to adjust the reconstituted products to exactly 12° Brix and to have all the samples at the same temperature before tasting. Products were rated in flavor in order of personal preference by members of the laboratory panel. Some of the lots were tasted by representatives from industry.

RESULTS AND DISCUSSION

Quantities collected. The quantities of essence and trap condensates obtained from 10 gallons of juice are shown in Table 1. The volumes of the essence frac-

TABLE 1

Volumes of fractions obtained from 10 gallons of juice

Juice used	Vaporization	Volume of essence from column	Volume of condensate in dry ice traps
Whole fruit puree:	%	ml.	ml.
First pass.....	11.3	285	95
Second pass.....	14.9	318	58
Machine-reamed:			
First pass.....	8.2	280	37
Second pass.....	7.4	240	31
Hand-reamed:			
First pass.....	15.9	132	65
Second pass.....	14.1	178	62
Free of peel oil:			
First pass.....	10.5	310	90
Second pass.....	10.5	432	76

tions were under the control of the operator. It will be noted that the trap condensates are greater in volume with the first pass. This is believed due to the deaeration that took place then which caused an increased quantity of noncondensable gases to be drawn through the traps. Other variations in the volumes recovered in the dry ice traps are primarily caused by different amounts of air leakage in different runs.

Recoverable peel oils. The data on oil recovery are given in Table 2. With the very high recoverable oil contents of the puree, the main oil recovery was in the decanters of the essence recovery unit, but in the other cases, the oil was found in the dry ice traps. These results indicate that in normal concentrations, peel oil would be a difficult constituent to recover under vacuum in the presence of even small quantities of water vapor.

TABLE 2
Oil recoverable from 10 gallons of orange juice

Juice type	Oil in juice	Oil recovered in essence decanters	Oil recovered in dry ice traps	Oil in stripped juice
Whole fruit puree:	%	ml.	ml.	%
First pass.....	0.88	95	7	0.56
Second pass.....	0.56	21	7	0.54
Machine-reamed:				
First pass.....	0.024	0	3.5	0.006
Second pass.....	0.006	0	2.5	0.004
Hand-reamed:				
First pass.....	0.006	0	3
Second pass.....	0	2
Free of peel oil:				
First pass.....	0.004	0	2
Second pass.....	0	1

Odor strength. In Table 3, data on the odor strength of the 2 fractions in the first and second passes from given juices are presented. In each case, the trap fraction in the first pass was the most potent. Next in potency came either the first pass essence or second pass dry ice trap condensates. Usually the second pass essence was the least potent.

TABLE 3

Relation between odor strength in fractions^a

Juice used	First pass		Second pass	
	Essence	Traps	Essence	Traps
Whole fruit puree.....	0.6	1.0	0.5	0.4
Machine-reamed.....	0.6	1.0	0.4	0.9
Hand-reamed.....	0.6	1.0	0.3	0.3
Free of peel oil.....	0.4	1.0	0.2	0.5

^a Horizontal comparisons by groups. The sample of each group judged most potent by the panel is arbitrarily assigned a value of 1.0.

When direct comparison was made between essence derived from a juice free of peel oil of 0.004% recoverable oil and a peel oil emulsion of 0.004% oil, the threshold dilution method showed that the emulsion was 80% as strong as the essence. There is some indication of an aroma in addition to that of peel oil. Comparisons of essence from juice of 0.006% recoverable oil and peel oil emulsion of 0.006% oil showed the emulsion to be 20% stronger. A similar comparison at an oil level of 0.024% showed the emulsion to be 5 times as strong as the essence. It should be pointed out that the substantial amounts of peel oil vaporized and collected in the dry ice traps did not enter into the comparisons. Higher ratings for the oil emulsions would be expected at these levels. Using juice from the Valencia rather than the Pineapple variety and an oil level of 0.0015%, the emulsion was only 30% as strong as the essence.

In Table 4, estimations have been made of the total aromatic materials collected in the complete fraction. While the dry ice trap products were of the greatest concentrations, greater amounts were recovered in the essences from the fractionating column. These values were again arbitrarily designated as 1.0. Essence recovered in the second pass averaged around two-thirds of the amounts from the first pass. Obviously 10% vaporization is insufficient to recover all the essence.

TABLE 4
Relation between total odorous materials present in fractions^d

Juice used	First pass		Second pass	
	Essence	Traps	Essence	Traps
Whole fruit puree.....	1.0	0.5	1.0	0.1
Machine-reamed.....	1.0	0.2	0.6	0.2
Hand-reamed.....	1.0	0.9	0.8	0.3
Free of peel oil.....	1.0	0.8	0.6	0.4

^d Horizontal comparisons by groups. The sample of each group judged most potent by the panel is arbitrarily assigned a value of 1.0.

In Table 5, the amounts of odorous material are compared in accordance with the kind of juice used. Of the essences recovered from the column in the first pass, the largest quantity was obtained from the machine-reamed juice; somewhat less from the hand-reamed juice, and the juices free of peel oil and a comparatively small amount of odorous material from the whole fruit puree. A considerable amount of oil separated in the traps when the whole fruit puree was run, suggesting the possibility that a considerable quantity of the aromatic materials were preferentially dissolved in the oil, leaving the water layers depleted. In the second pass of this last run, less oil was present and the relative rating of the essence was higher. The results with the machine-reamed juice, the hand-reamed juice, and juice free of peel oil, show somewhat more potent water-soluble essences with higher peel oil content, but the differences were not great.

TABLE 5
Relation between odorous materials and methods of extraction^e

Juice used	First pass		Second pass	
	Essence	Traps	Essence	Traps
Whole fruit puree.....	0.5	0.5	1.0	0.3
Machine-reamed.....	1.0	0.4	0.9	0.3
Hand-reamed.....	0.6	1.0	0.5	1.0
Free of peel oil.....	0.5	0.8	0.8	0.7

^e Vertical comparisons by groups. The sample of each group judged most potent by the panel is arbitrarily assigned a value of 1.0.

The essence obtained from the 0.010% coldpressed peel oil emulsion was very similar in types of odor present to that obtained from fresh juice of 0.006% oil content (hand-reamed) but lacking somewhat in flowery odors. The strength was less by about $\frac{1}{3}$. The potency of the water-soluble essence from the 0.050% peel oil emulsion appeared to be less than the 0.010% emulsion, again possibly due to the amount of peel oil separating in the first decanter, and the previously mentioned preferential solubility of odorous material in the oil layer.

A coldpressed peel oil emulsion of 0.044% oil content was 85% as strong as the orange juice of 0.044% recoverable oil content. This indicates peel oil to be the principal constituent contributing to the aroma, but possibly not all.

Effectiveness in restoring aroma. A comparison of reconstituted concentrate with added essence and without essence showed that the presence of essence did contribute to orange aroma. There was some difference of opinion in comparing desirability of products with coldpressed peel oil only and those with both essence and peel oil. Some individuals expect and look for a

fairly strong peel oil taste, while others prefer milder oily taste and tend to favor the essence. The consensus of the laboratory taste panel was that essence, when freshly added, complemented the taste of coldpressed peel oil and made it approach the fresh natural flavor of oranges, but not as closely as when cut-back juice was used.

A large variation was observed in recoverable peel oil content of juices prepared by the method of Blair (3). Oil content varied from 0.004 to 0.00066%. This variation is apparently due to differences in variety and maturity of the fruit.

The stability of the water-soluble essence in orange concentrate was not satisfactory. Even in storage at 0° F. (−17.8° C.) in 4-fold concentrates, the essences left no detectable aroma at the end of 6 months. A residual effect of the heightening of the peel oil flavor was noted. The aroma of peel oil did not seem to be materially affected during this storage. Additional studies are being undertaken to test this point. In no case was the development of an "apricot-like" or other off-flavor noted during storage from the use of the water-soluble essences as reported by some. It is thought possible that the "apricot-like" flavor reported by others may be due to the absence of some odorous material, most likely a peel oil fraction. The methods used by Rice *et al.* (15) and Kaufman and Campbell (8) would tend to give products with very little peel oil. Previously, when canned single-strength orange juices were prepared at this laboratory by the method of Blair (3), juices of very low recoverable oil contents were obtained (0.001% and lower). The flavor and aroma of these juices were not well balanced and were described by some as "apricot like."

SUMMARY

A system for the recovery of water-soluble essences under vacuum at temperatures of 110-115° F. (43.3°-46.1° C.) has been developed and applied to orange juice. The orange juice is not noticeably deteriorated by processing at this temperature. With this equipment it is necessary to evaporate at least 20% of the juice in order to obtain the bulk of the essence.

A relation was found between the aroma of the essence and peel oil content. In the range of 0.004 to 0.024% recoverable oil, slightly more potent water-soluble essences were obtained with larger amounts of peel oil, but not proportionally. An orange peel oil emulsion in water also gave an essence somewhat similar to the essence from whole orange juice.

While the bulk of the water-soluble materials were collected from condensers cooled with ice water, dry ice traps were necessary to retain the peel oil when juices of 0.024% recoverable oil contents or under were used. Some water-soluble essence was also obtained in these traps.

The use of the water-soluble essence enhanced the floral character of the aroma of the freshly prepared concentrate and reconstituted product, but this aroma was lost in 6 months even with storage at 0° F. (−17.8° C.). A residual heightening of the peel oil flavor remained, but no off-flavors were formed.

LITERATURE CITED

1. BEAVENS, E. A. New frozen purees from citrus fruits. U. S. Bur. Agr. Ind. Chem., *AIC-238* (1949).
2. BISSETT, O. W. Frozen puree from Florida citrus fruits. *Proc. Fla. State Hort. Soc.*, **62**, 16 (1949).
3. BLAIR, J. S., GODAR, E. M., MASTERS, J. E., AND RIESTER, D. W. Exploratory experiments to identify chemical reactions causing flavor deterioration during storage of canned orange juice. I. Incompatibility of peel-oil constituents with the acid juice. *Food Research*, **17**, 235 (1952).
4. ESKEW, R. K., HOMILLER, R. P., AND PHILLIPS, G. W. M. Process for making frozen concentrated fruit juices. U. S. Patent 2,573,699 (Nov. 6, 1951).
5. ESKEW, R. K., PHILLIPS, G. W. M., HOMILLER, R. P., AND EISENHARDT, N. H. Preparation of full-flavor frozen grape juice concentrates. U. S. Bur. Agr. Ind. Chem., *AIC-301* (1951).
6. ESKEW, R. K., PHILLIPS, G. W. M., HOMILLER, R. P., REDFIELD, C. S., AND DAVIS, R. A. Frozen concentrated apple juice. *Ind. Eng. Chem.*, **43**, 2397 (1951).
7. HALL, J. A., AND WILSON, C. P. The volatile constituents of Valencia orange juice. *J. Am. Chem. Soc.*, **47**, 2575 (1925).
8. KAUFMAN, C. W., AND CAMPBELL, H. A. Some fundamental considerations in the processing of frozen orange juice concentrate. *Food Technol.*, **3**, 395 (1949).
9. KIRCHNER, J. G., RICE, R. G., MILLER, J. M., AND KELLER, G. J. The presence of hydrogen sulfide in citrus juices. *Arch. Biochem.*, **25**, 231 (1950).
10. MACDOWELL, L. G., MOORE, E. L., AND ATKINS, C. D. Method of preparing full-flavored fruit juice concentrates. U. S. Patent 2,453,109 (Nov. 9, 1948).
11. MILLEVILLE, H. P., AND ESKEW, R. K. Recovery of volatile apple flavors in essence form. *Western Canner & Packer*, **38** (11), 51 (Oct. 1946).
12. MONCRIEF, R. W. *The Chemical Senses*. 1946, John Wiley & Sons, Inc., New York.
13. NELSON, E. K., AND MOTTERN, H. H. The occurrence of citral in Florida Valencia orange oil. *J. Am. Chem. Soc.*, **56**, 1238 (1934).
14. POORE, H. D. Analysis and composition of California lemon and orange oils. U. S. Dept. Agr., *Tech. Bull.* No. 241 (1932).
15. RICE, R. G., KELLER, G. J., AND BEAVENS, E. A. Flavor fortification of California frozen orange concentrate. *Food Technol.*, **6**, 35 (1952).
16. WALKER, L. H., NIMMO, C. C., AND PATTERSON, D. C. Preparation of frozen apple juice concentrate. *Food Technol.*, **5**, 148 (1951).